Evaluation of Laser-Based Analysis of REE in Coal-Related Materials

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Analytical Methods

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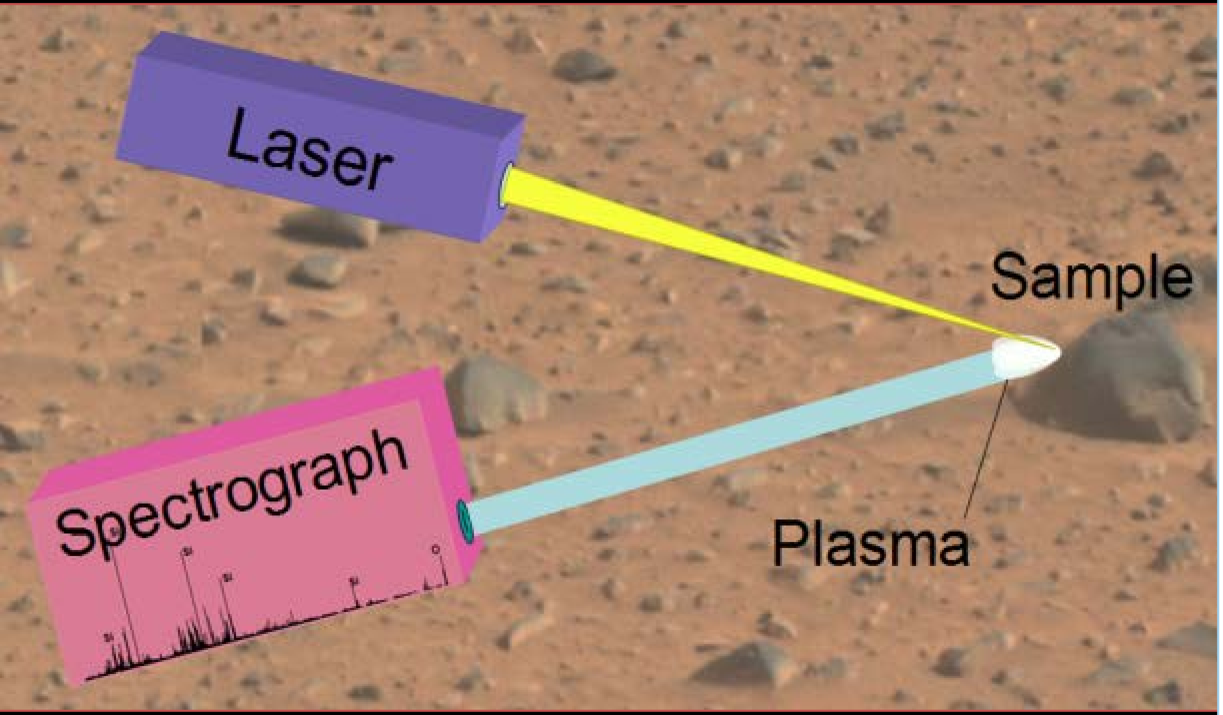
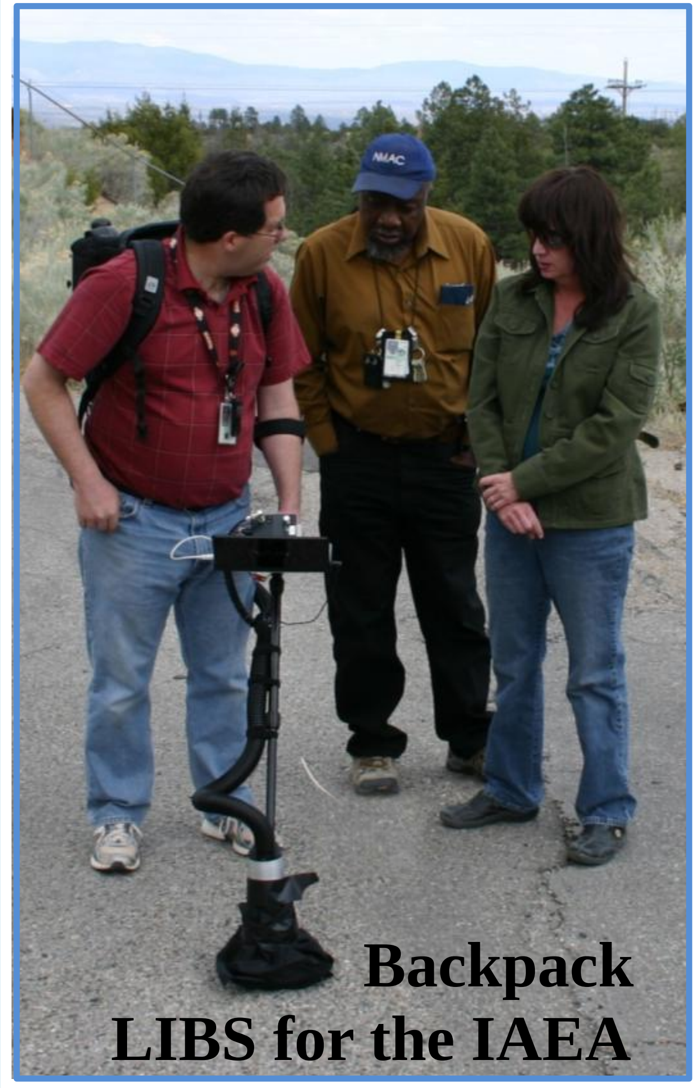
- Laser-Induced Breakdown Spectroscopy (LIBS)
  - Elemental Analysis
  - Develop and Test Multivariate Analysis Calibration
  - Estimate Detection Limits
- Raman Spectroscopy
  - Mineralogical Analysis
- Field demonstration of a breadboard instrument
  - Designed from laboratory LIBS and Raman investigations above
  - No Sample Preparation Required

Laser-Induced Breakdown Spectroscopy (LIBS)



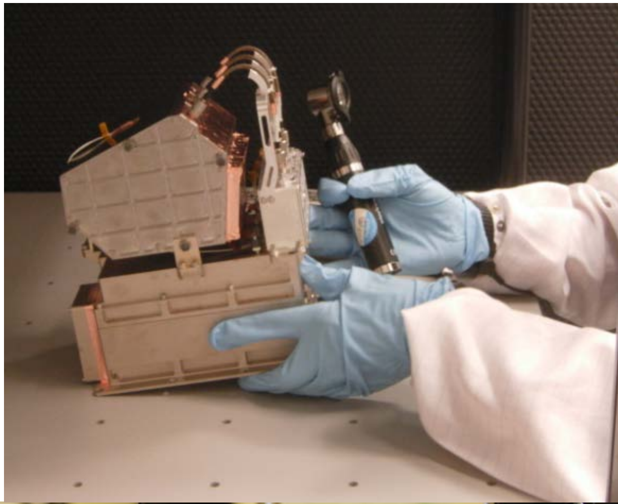


Aluminum Copper Basalt

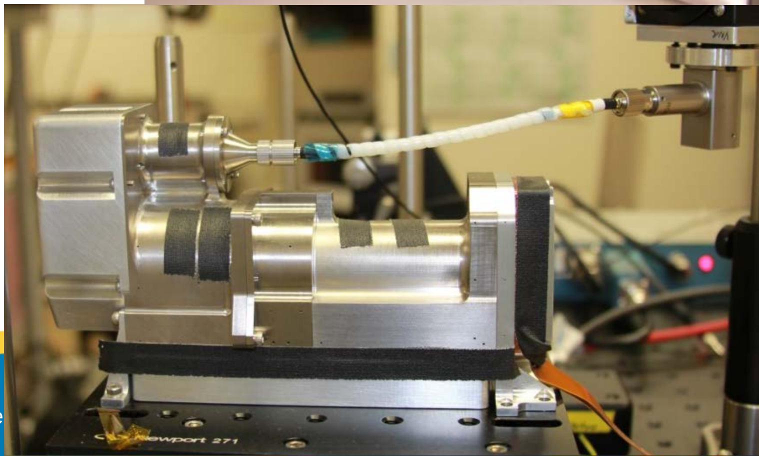
Sirven et al., JAAS

LIBS and Raman Instrumentation

- LIBS instrument development started with Ocean Optics Spectrometers
  - Readout noise limited detectors
  - Not gated detectors
- ChemCam Instrument – LIBS only
  - Based on Ocean Optics Spectrometer design, significantly better, more expensive detectors
  - Still not gated.



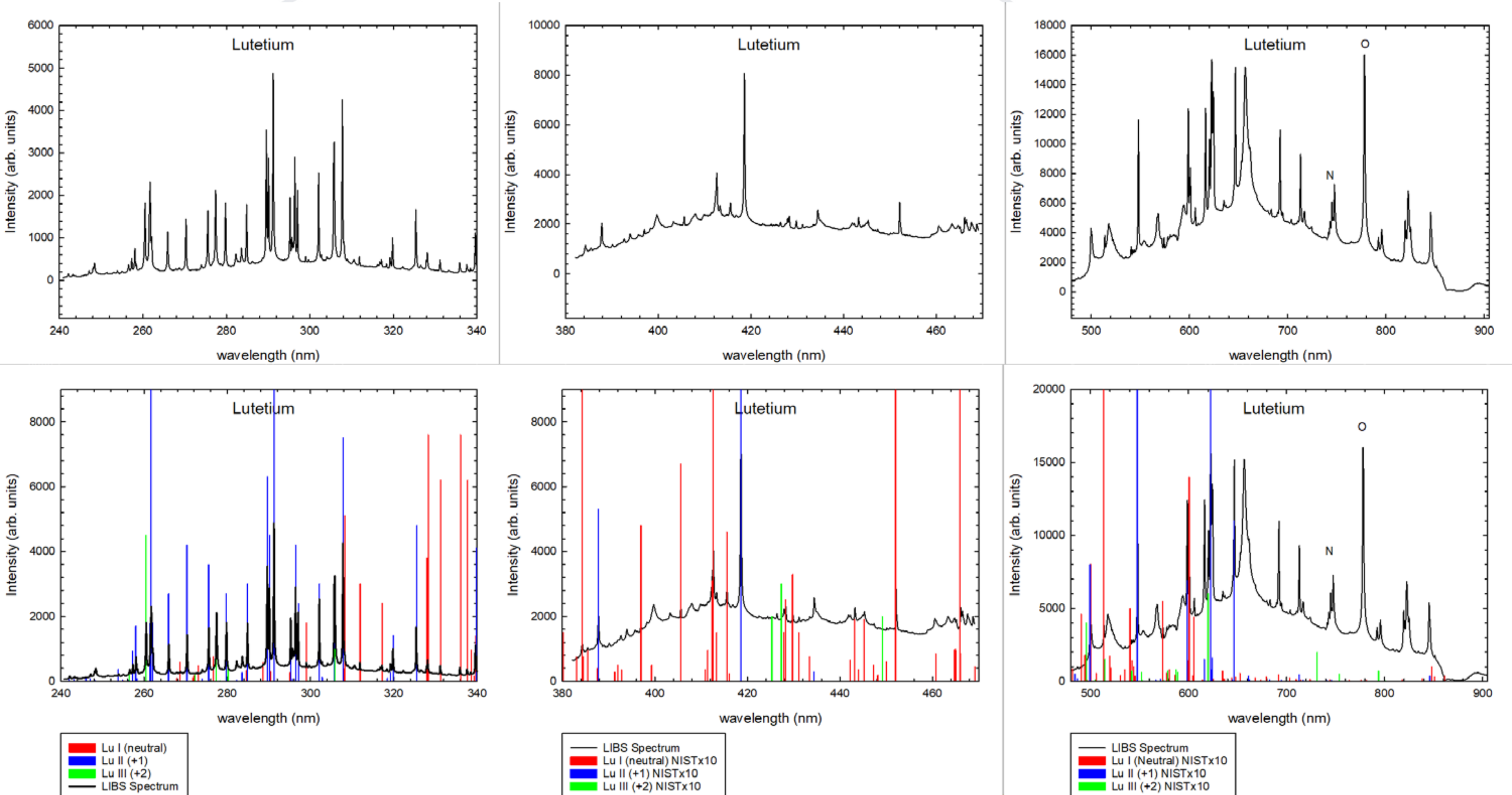
- LDRD DR Developed Raman-LIBS Spectrometer (RLS)
  - Same detectors used in ChemCam
  - Gated detectors
- SuperCam – Raman and LIBS
- VEMCam – Venus Raman and LIBS



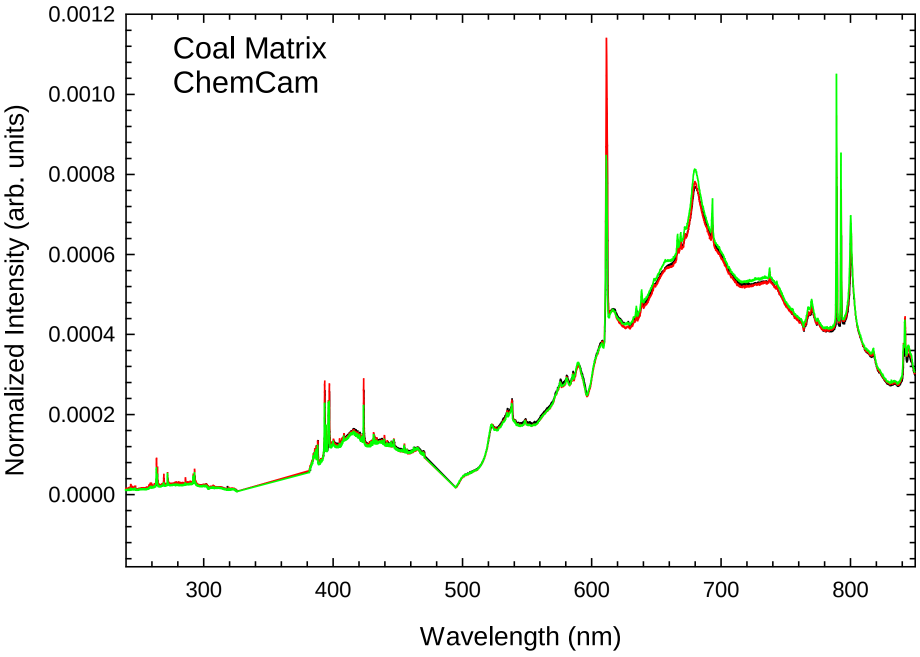
Samples

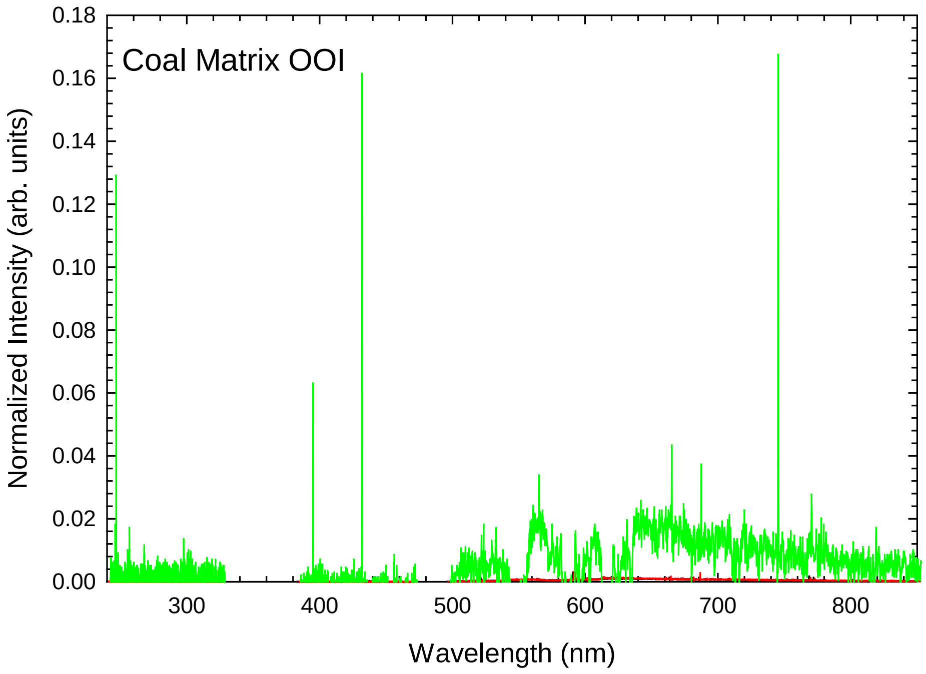
- LIBS Spectral Libraries
  - Spectra for each pure REE
  - Identify emission lines in LIBS spectra
- Calibration
  - 28 Samples Prepared
  - Coal Matrix
  - Between 1 and 5 REEs in each sample

REE Library Spectra (ChemCam)



Calibration Spectra
ChemCam vs. Ocean Optics



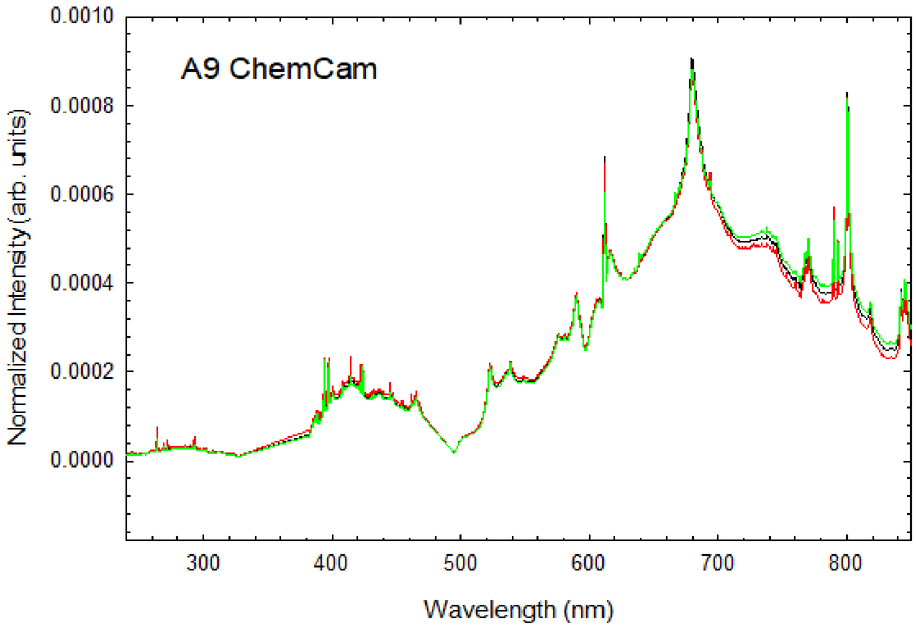


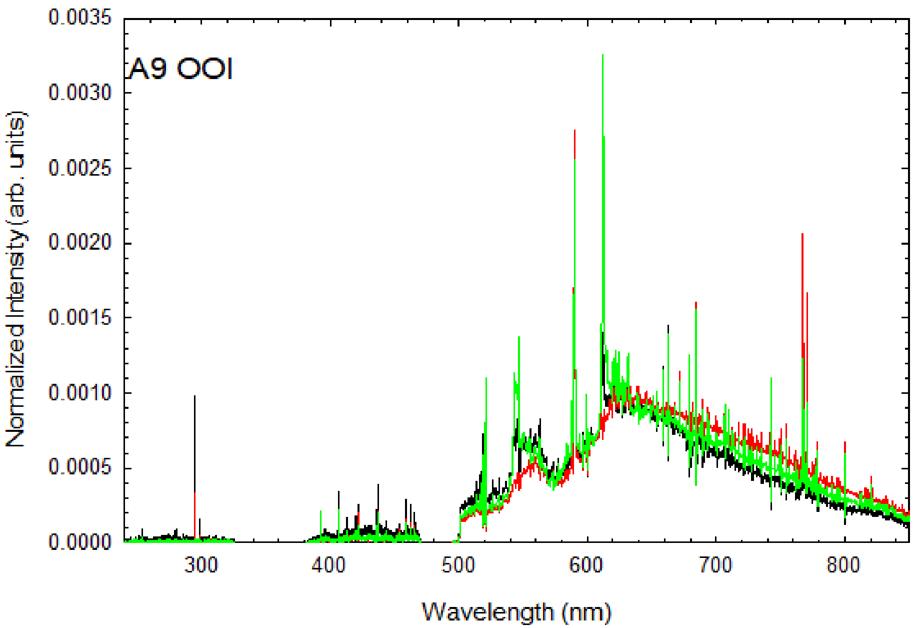
1.5 m standoff distance

5 cm standoff distance

Ocean Optics spectrometers are not adequate for this analysis.

Calibration Spectra
ChemCam vs. Ocean Optics





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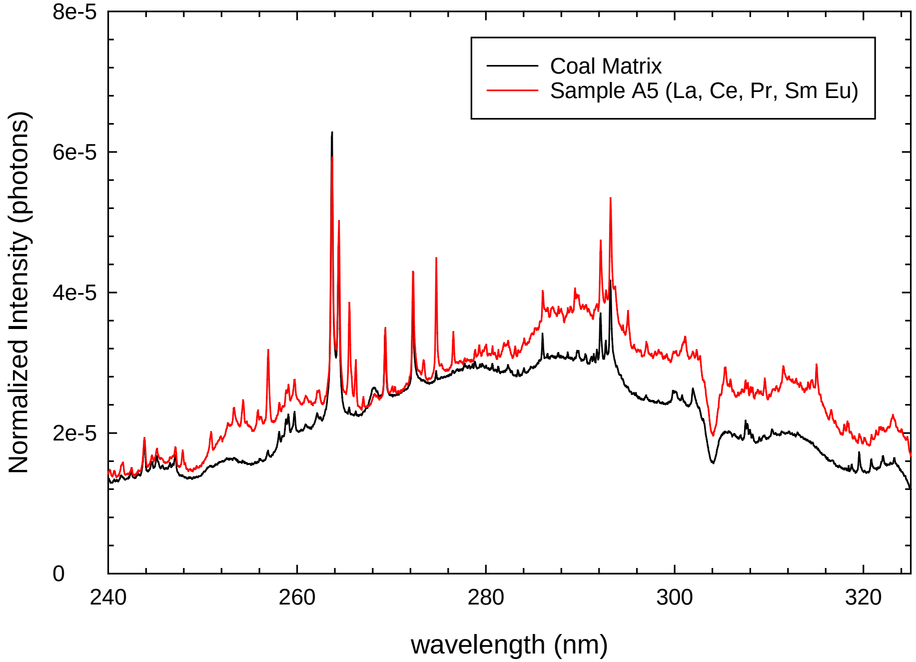
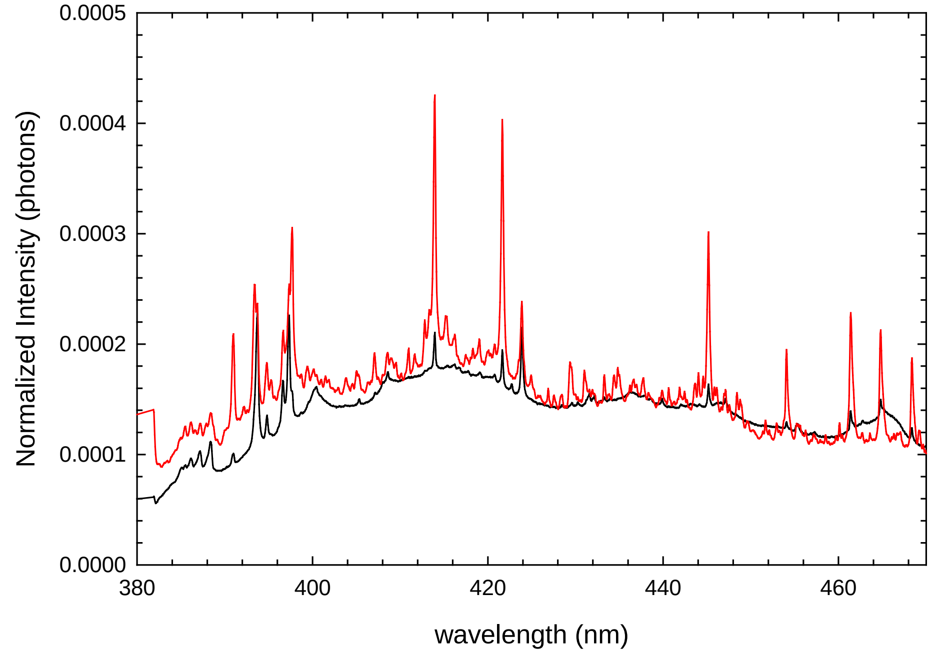
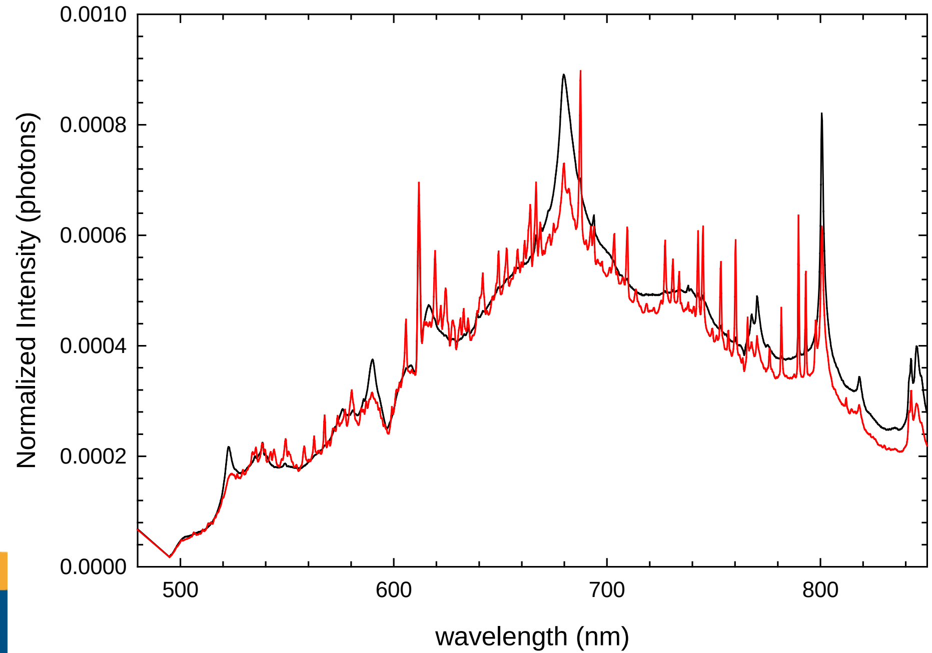
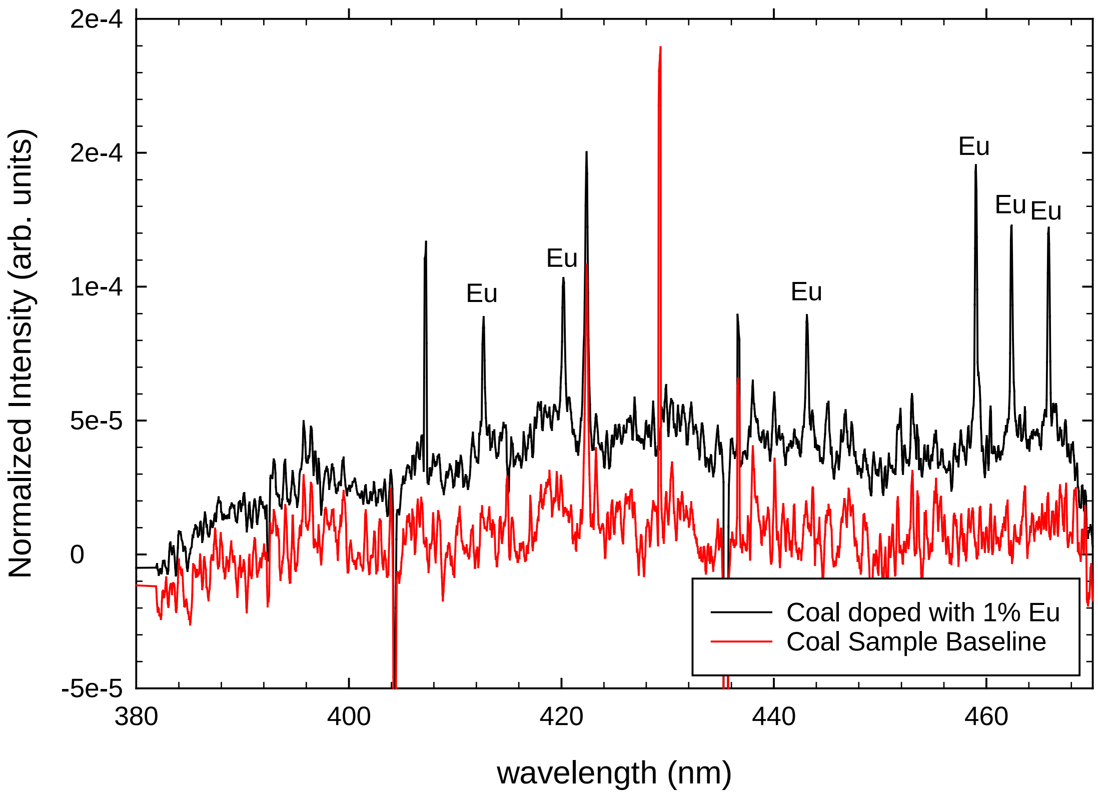
Coal Matrix vs. Doped Sample



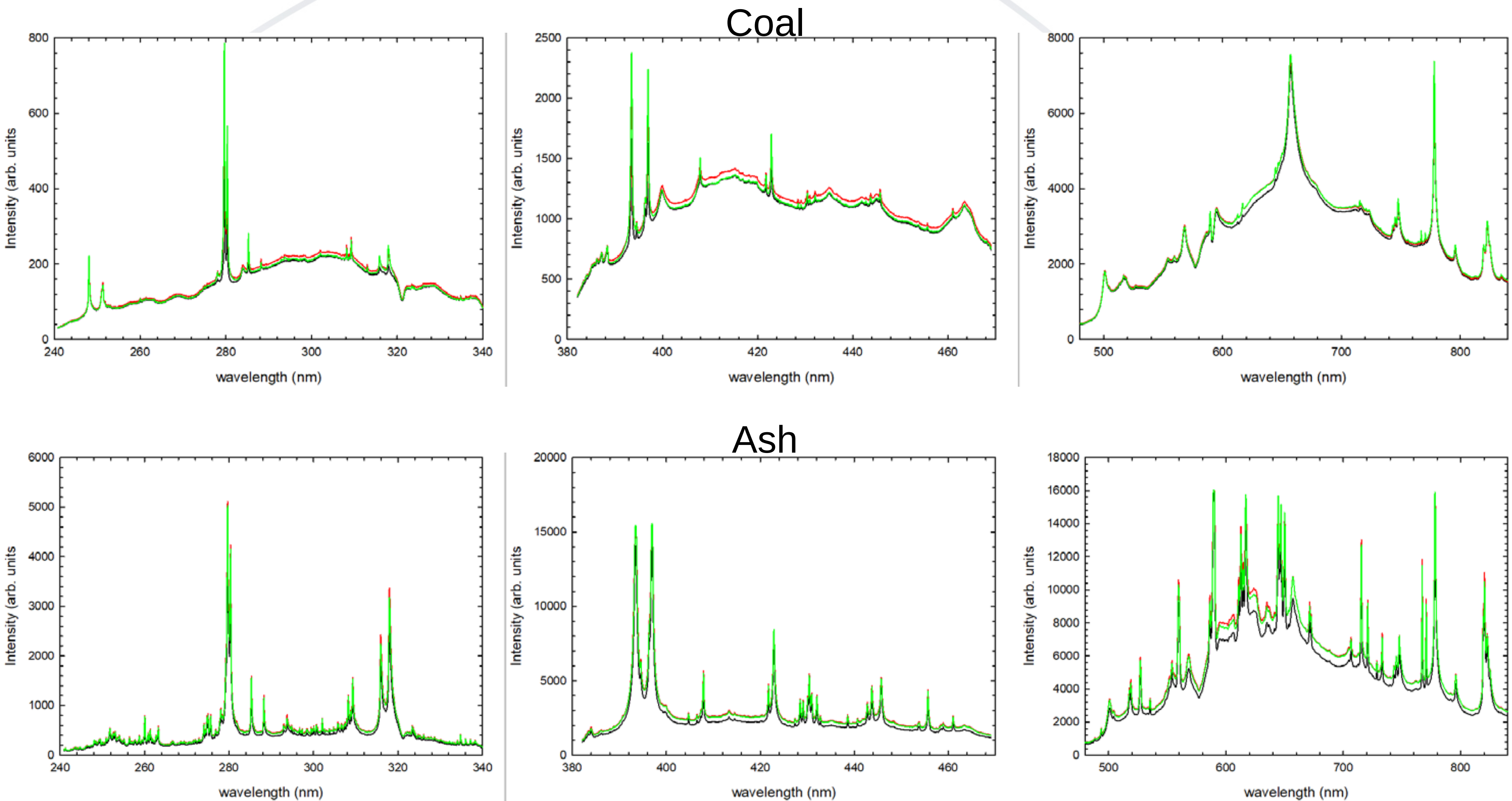




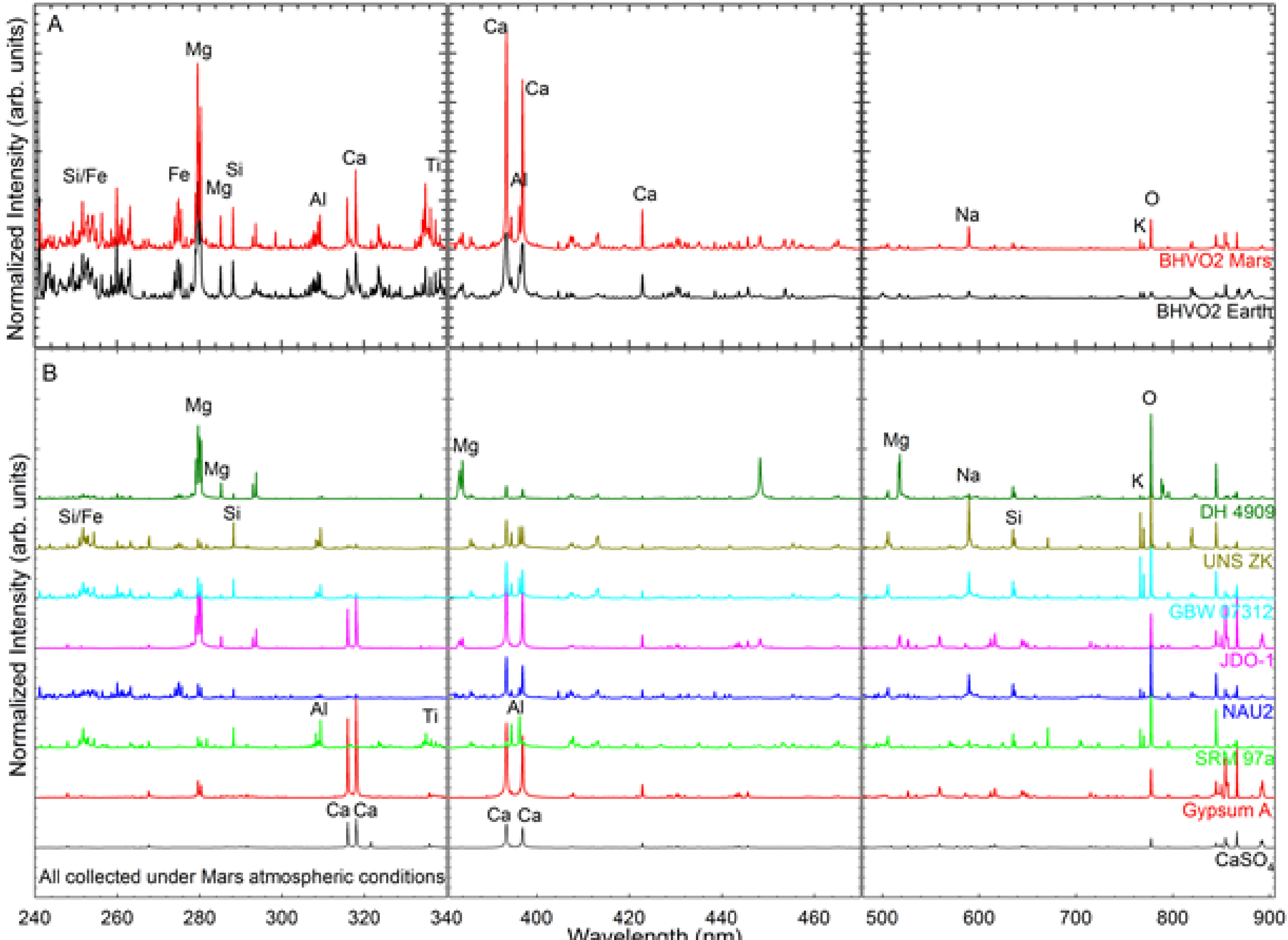
Coal with 1% Eu



Coal vs. Ash LIBS Spectrum



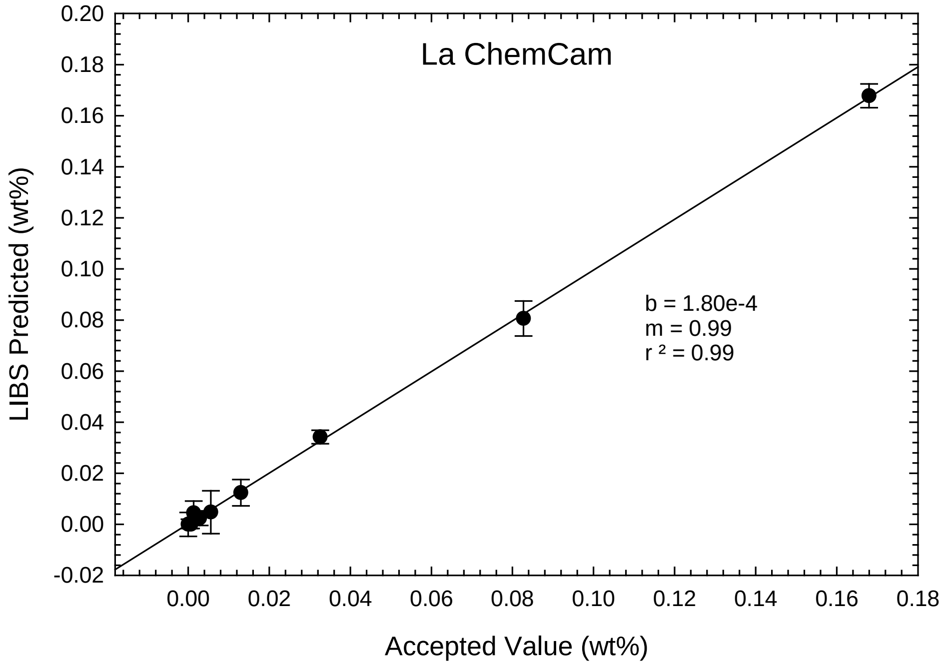
Typical Geochemical Samples

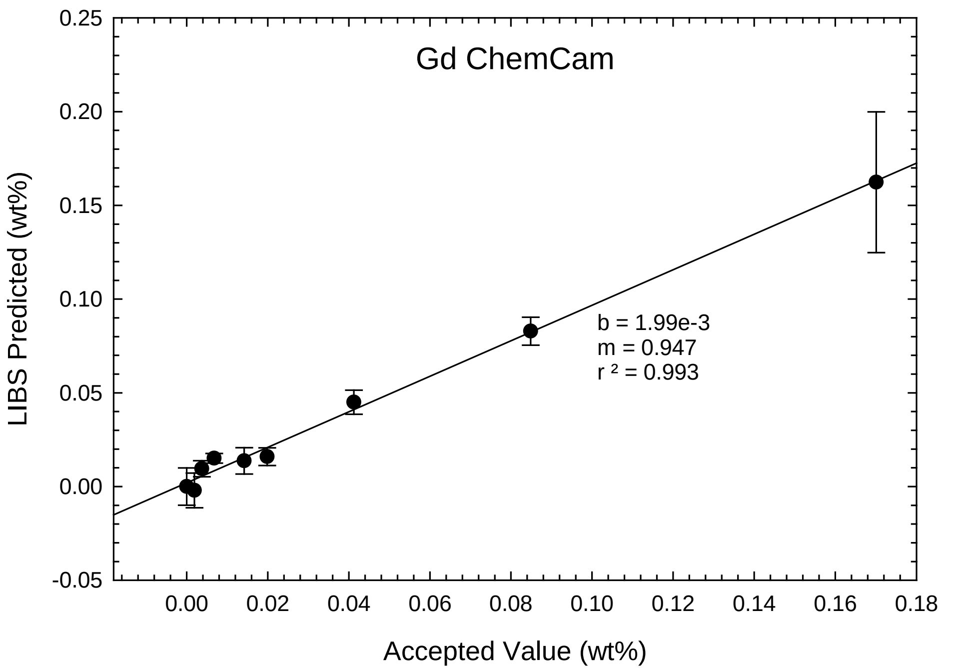


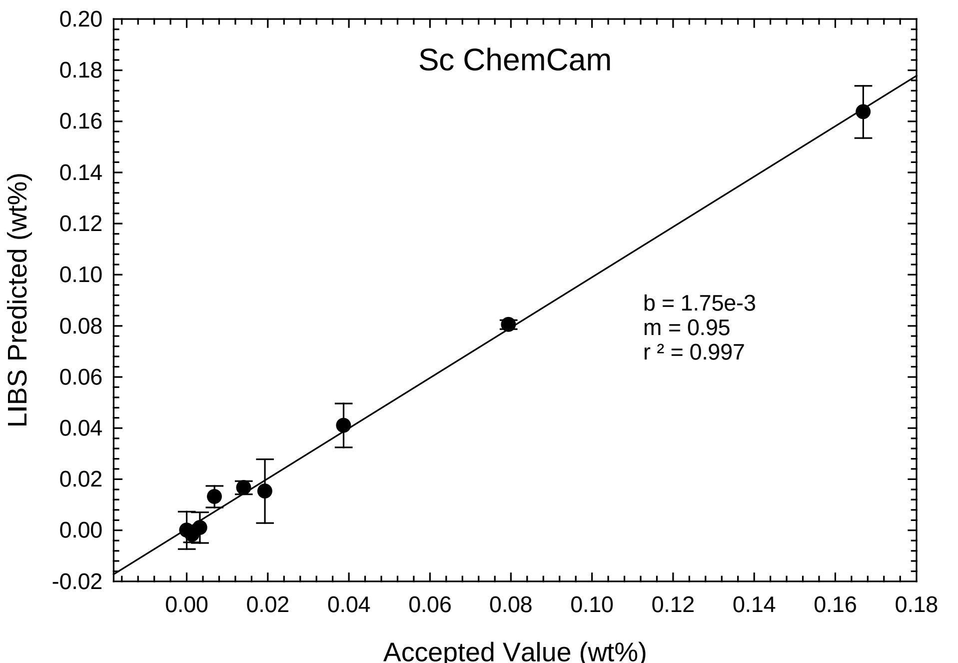
Calibration Analysis

- Partial Least Squares (PLS)
  - PySAT Program developed by Anderson (USGS) and Clegg
  - Used to develop calibrations for ChemCam and SuperCam
  - Leave one target out analysis
    - One target is treated as an unknown
    - Repeated for all targets
- Variables
  - X: LIBS Spectra, all wavelength channels
  - Y: Concentrations
- Developed 15 separate PLS models
- Uncertainty Analysis
  - 3 replica measurements per sample
- Estimate detection limits (conservative and likely)

Calibration Curves







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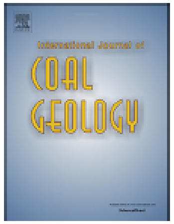

Evaluation of trace elements in U.S. coals using the USGS COALQUAL database version 3.0. Part I: Rare earth elements and yttrium (REY)

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ABSTRACT

Coal is a potential source of valuable elements such as rare earth elements and yttrium (REY). In this work, REY concentrations in U.S. domestic coals were evaluated using data from the USGS COALQUAL Database Version 3.0. The database contains a total of 7657 non-weathered, full-bed coal samples. The number of samples containing REY data points varies among elements. Assessment of data quality indicates that some of the REY data are semi-quantitative and should be used with caution. Different analytical instruments and methods with varying accuracies and precisions are thought to be the main sources of errors. Inclusion of qualified data also accounts for the sawtooth pattern of the UCC-normalized REY distribution. A new set of Q factor values was thus proposed to adjust qualified data. Consequently, mean concentrations of REY in U.S. coals were obtained with a total REY concentration of 65.5 ppm on a moisture-free whole coal basis. Further evaluation of REY in 5378 selected coal samples indicates that about 9–13% of the samples fall into the combined category of promising and highly promising coals for REY, according to the classification of Dai et al. (2017). Taking sampling bias into consideration, we further found that bituminous coal, particularly from the central Appalachian region, has the highest probability of being a source for beneficial recovery of REY. More specifically, bituminous coal from eastern Kentucky is likely to be the best option. Finally, we conclude that U.S. domestic coal is a promising, alternative source for beneficial recovery of REY to meet the U.S. REY demand for economic growth.

Detection Requirements for Instrument Design

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Table 2

A summary of REY data from the USGS COALQUAL V3.0 database (Concentrations in ppm on a moisture-free whole coal basis).

Element	Include data with L qualifier				Exclude data with L qualifier				Data with L qualifier			From Finkelman (1993)[a]			
	No. of samples	Max	Mean[b]	SD[c]	No. of samples	Max	Mean	SD	No. of samples	%L[d]	Mean	No. of samples	Max	Mean	SD
Y	7585	185	8.93	6.84	7560	185	8.94	6.83	25	0.3	4.92	7897	170	8.5	6.7
La	6652	236	11.70	9.42	6160	236	11.19	9.06	492	7	18.10	6235	300	12	16
Ce	6081	506	23.96	25.45	5557	506	20.69	17.42	524	9	58.68	5525	700	21	28
Pr	5601	110	10.21	8.33	948	67.5	6.48	7.32	4653	83	10.97	1533	65	2.4[e]	n/a[g]
Nd	5946	236	12.32	11.09	4303	236	13.36	11.76	1643	28	9.60	4749	230	9.5[f]	n/a
Sm	5588	68	2.54	3.78	5103	19.9	1.94	1.42	485	9	8.87	5151	18	1.7	1.4
Eu	5626	5.83	0.42	0.28	5270	5.83	0.43	0.28	356	6	0.32	5266	4.8	0.4	0.33
Gd	5602	39.7	2.91	2.39	1670	39.7	2.80	2.75	3932	70	2.96	2376	39	1.8[f]	n/a
Tb	5619	47	1.16	3.76	4878	4.08	0.33	0.22	741	13	6.57	5024	3.9	0.3	0.23
Dy	5607	23	3.11	2.15	717	19.2	3.39	2.46	4890	87	3.07	1510	28	1.9	2.7
Ho	5598	19	1.03	1.06	351	4.59	0.75	0.56	5247	94	1.05	1130	4.5	0.35[f]	n/a
Er	5603	16	1.24	0.95	1070	11.2	1.54	1.08	4533	81	1.17	1792	11	1	1.1
Tm	5603	7.7	0.63	0.48	42	1.99	0.44	0.41	5561	99	0.63	365	1.9	0.15[f]	n/a
Yb	7269	9.27	1.01	0.68	7222	9.27	1.02	0.68	47	1	0.50	7522	20	0.95[f]	n/a
Lu	5587	10.1	0.37	0.89	4945	10.1	0.16	0.24	642	11	1.99	5006	1.8	0.14	0.1

[a] Data obtained from the NCRDS before the release of the COALQUAL database.
[b] Mean: arithmetic mean.
[c] SD: standard deviation.
[d] Percent of data with L qualifier.
[e] Estimated based on NCRDS and literature data.
[f] Calculated from La and Ce data assuming a smooth chondrite-normalized REE distribution pattern with the exception of Eu.
[g] No data available.

REE Elemental Detection Limits Estimates vs. Requirements

	Requirements (ppm)		LIBS DL (ppm)	
Elements	Max	Mean	Conservative	Likely
Y	185	8.94	Not in study	
La	236	11.19	100	10
Ce	506	20.69	150	15
Pr	67.5	6.48	70	5
Nd	236	13.36	200	10
Sm	19.9	1.94	60	4
Eu	5.83	0.43	50	5
Gd	39.7	2.8	60	5
Tb	4.08	0.33	50	4
Dy	19.2	3.39	20	3
Ho	4.59	0.75	40	1
Er	11.2	1.54	20	2
Tm	1.99	0.44	30	2
Yb	9.27	1.02	20	1
Lu	10.1	0.16	20	1

- Design instrument to meet requirements (Lin et al.)
- In situ analysis, not remote like ChemCam
- Obtain more certified calibration standards
  - Requires correct matrix
- Sampling protocol

Summary

- LIBS can detect all REEs with a coal matix
  - Detection limits specified by Lin et al. should be achievable in a field deployable instrument.
- A gated detector would significantly improve the detection limits and quantitative analysis
  - Ocean Optics spectrometers could be used but probably would not realize the required detection discussed in Lin et al.
- REE Mineralogy will be determined by Raman spectroscopy
  - Also requires gated detector.

Backup

AGU PUBLICATIONS

JGR

Journal of Geophysical Research: Planets

RESEARCH ARTICLE

10.1002/2016JE005201

Key Points:

- Revised Li, Sr, Rb, and Ba abundances have been obtained with updated univariate calibrations
- The trace element abundances of alkaline and magnesian rocks are similar to the composition of monzonitic and basaltic clasts in NWA7533
- Alkali trace element enrichments are associated with K-bearing

Alkali trace elements in Gale crater, Mars, with ChemCam: Calibration update and geological implications

V. Payré[1], C. Fabre[1], A. Cousin[2], V. Sautter[3], R. C. Wiens[4], O. Forni[2], O. Gasnault[2], N. Mangold[5], P.-Y. Meslin[2], J. Lasue[2], A. Ollila[4], W. Rapin[2], S. Maurice[2], M. Nachon[6], L. Le Deit[5], N. Lanza[4], and S. Clegg[4]

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Table 2. Summary Table of Li, Sr, Rb, and Ba Quantifications of ChemCam Data

	Input	Peak Fitting					Calibration Equation	Validity	RMSE (ppm)	LOD (ppm)
		Peak (nm)	Function	Baseline	Range (nm)	Deconvolution (nm)				
Li	Clean Calibrated Spectra[a]	670.97	Lorentz	Parabolic	669.9–674.0	Si: 670.12 Ca: 671.85	$y = 4.04\ E6\ x^2 + 34060x$	Area < 1.8 E − 3	5	5
Sr		421.67			421.4–422.3	Ca: 422.055	$y = 7.99\ E9\ x^2 + 17.16\ E5\ x$	Area < 4.0 E − 4	150	87
Rb		780.24			779.3–781.0	None	$y = 2.83\ E7\ x^2 + 27.77\ E4\ x$	Area < 1.2 E − 3	34	26
Ba		455.55			454.4–456.2	Ti: 454.6 455.09 455.68 Ti/Si: 455.35	$y = 3.74\ E9\ x^2 + 18.81\ E5\ x$	Area < 1.2 E − 3 $SiO_2 < 70$ wt %	334	120

[a]Clean Calibrated Spectra (CCS) are processed spectra as described in *Wiens et al.* [2013].